

AN INVESTIGATION OF THE EXISTENCE
OF A SODIUM LITHIUM MOLECULE

by

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INTRODUCTION

From the literature it is found that the vapors of the alkali metals have been examined for absorption and magnetic rotation rather extensively. It has been established from their characteristic band absorption that these metals form diatomic molecules not only in the case of molecules formed from single element vapors, but also in the case of molecules formed in the vapors of combinations of two separate alkali metals. Walter and Barratt (1) examined and identified the absorption spectra of Li_2 , Na_2 , K_2 , Rb_2 , and Cs_2 . They then examined combinations of these metals and identified band structure of LiK , LiRb , LiCs , NaK , NaRb , NaCs , KRb , RbCs , and KCs . Higher and more complete analysis has been carried out in the case of Li_2 (2, 3, 4, 5), Na_2 (6, 7, 8, 9), Cs_2 (10), NaK (11), Rb_2 and NaRb (12). To date, a band system identifiable as due to a NaLi absorption has not been found. Walter and Barratt (1) attempted to detect such a molecule but did not. They attributed the failure to the fact that much of the spectrum in the region of the visible, near infra red, and ultra violet is covered with the band systems of Na_2 and Li_2 . Sodium has two prominent band systems--one in the blue green and a second in the red. A third system is evident (at higher pressures of the metallic vapors) falling near the second principal resonance line of sodium at approximately 3300 angstroms units. Lithium is characterized by two systems, one in the blue green and a second in the red. Thus, since a con-

siderable portion of the spectrum is covered by strong bands of sodium molecules and lithium molecules, new undetected band structure originating from a NaLi combination may be masked beneath the already existing absorption regions of Na_2 and Li_2 . This difficulty might be overcome by taking advantage of the fact that the concentration of the three molecules (i.e., Na_2 , Li_2 , and NaLi) are respectively proportional to the products of the concentration of the constituent atoms. By working with sodium with just a trace of lithium in the regions most heavily covered by the lithium bands and vice versa for the regions most heavily masked by the sodium bands, it is possible that a band system attributable to NaLi could be discovered.

The absorption band systems of Na_2 and Li_2 in each case involve transitions from a $^1\Sigma$ molecular ground level which dissociates into normal sodium and normal lithium atoms to excited molecular $^1\Sigma$ and $^1\Pi$ levels (8,4). Both of the upper levels dissociate into one normal atom and one in the resonance (P) state. The theory used by Loomis and Arvin (12) indicates that there should be four systems of NaLi bands in the visible and infra red. This is plausible since, besides the ground level which would dissociate into normal sodium and lithium atoms, there should be a pair of levels, $^1\Sigma$ and $^1\Pi$, dissociating into normal sodium and excited lithium and a similar pair dissociating into normal lithium and excited sodium. The four band systems would correspond to transitions between the ground level and the

four excited molecular levels.

This research work has been undertaken in an endeavor to find band structure(s), in absorption, of the NaLi molecule. If such a band system could be discovered it would allow further analysis to determine such items as the binding forces between the atoms, electron configuration in the molecule, heats of dissociation, dissociation products, internuclear distances, etc.

APPARATUS

A general view of the experimental apparatus is given on Plate I.

Vacuum System

The vacuum system consisted of a two stage mercury diffusion pump. To the rear of the system a bottle of neon gas was attached. Since a considerable amount of the work was done using only fore-pump evacuation, neon was used to flush the tube one or more times during evacuation. In this manner an excellent vacuum with reference to oxygen, water vapor, and etc., was easily accomplished.

Spectrographic Apparatus

The Bausch and Lomb small Littrow spectrograph evident in Plate I was used for preliminary examination of the absorption spectra. For further examination the furnace and absorption tube was detached at the wax joint indicated in Plate I and was

EXPLANATION OF PLATE I

A general view of the experimental apparatus.

A--Bausch and Lomb small Littrow spectrograph.

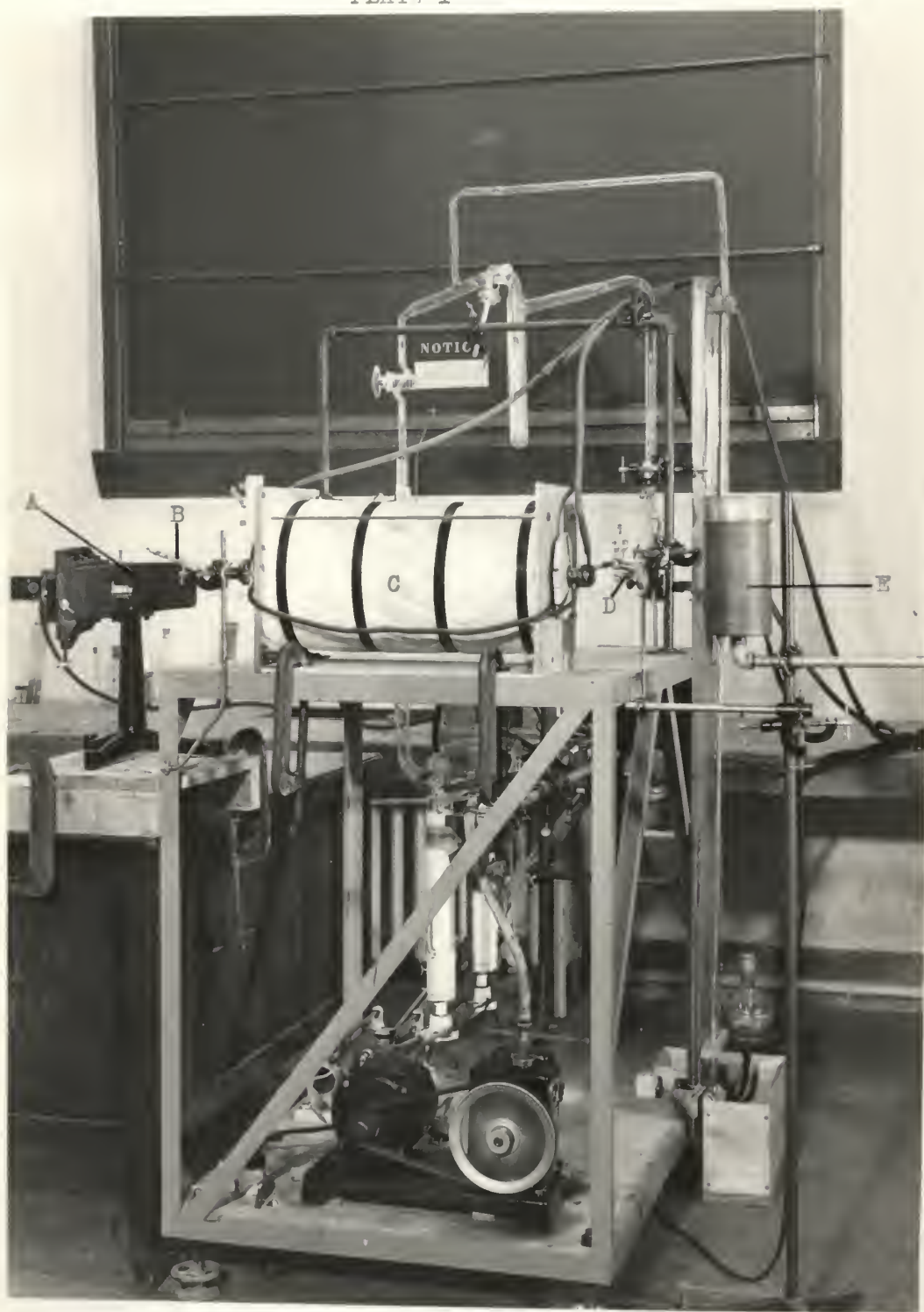
B--Sodium tube with asbestos covering.

C--Furnace.

D--Wax joint for disconnecting absorption tube from
the vacuum system.

E--Light source.

PLATE I



mounted before a Bausch & Lomb medium quartz spectrograph.

Both Eastman 50 and Eastman type I-N spectroscopic plates were used in the analysis. Eastman type I-N plates gave good sensitivity over the region beginning at approximately 2300 \AA and stretching well into the infra red. Eastman 50 plates gave satisfactory sensitivity in the region from 2100 \AA to 6700 \AA . The lithium 6707 \AA resonance line as well as the red band systems of the two elements did not appear on these latter plates and for this reason they were somewhat unsatisfactory. It was helpful to use plates showing the resonance lines as their intensities gave a relative measure of the constituent vapor pressures within the tube.

Optical System

To provide the continuous background for the absorption, a General Electric H-3 high pressure mercury arc was used. The continuum of the mercury discharge in this type lamp covers the range from the red to the ultra-violet. For background in which the chief concern was the red end of the spectrum, a 500 watt projection bulb proved very satisfactory. The projection bulb gave satisfactory exposures at wave lengths as low as 3500 angstrom units. Both of these sources gave intense illumination. Two quartz lenses, each of approximately ten centimeters focal length, were used to focus the light beam at the center of the tube and thence refocus on the slit of the spectrograph. With this type optical system, exposure time varied from one to five seconds.

Absorption Tube

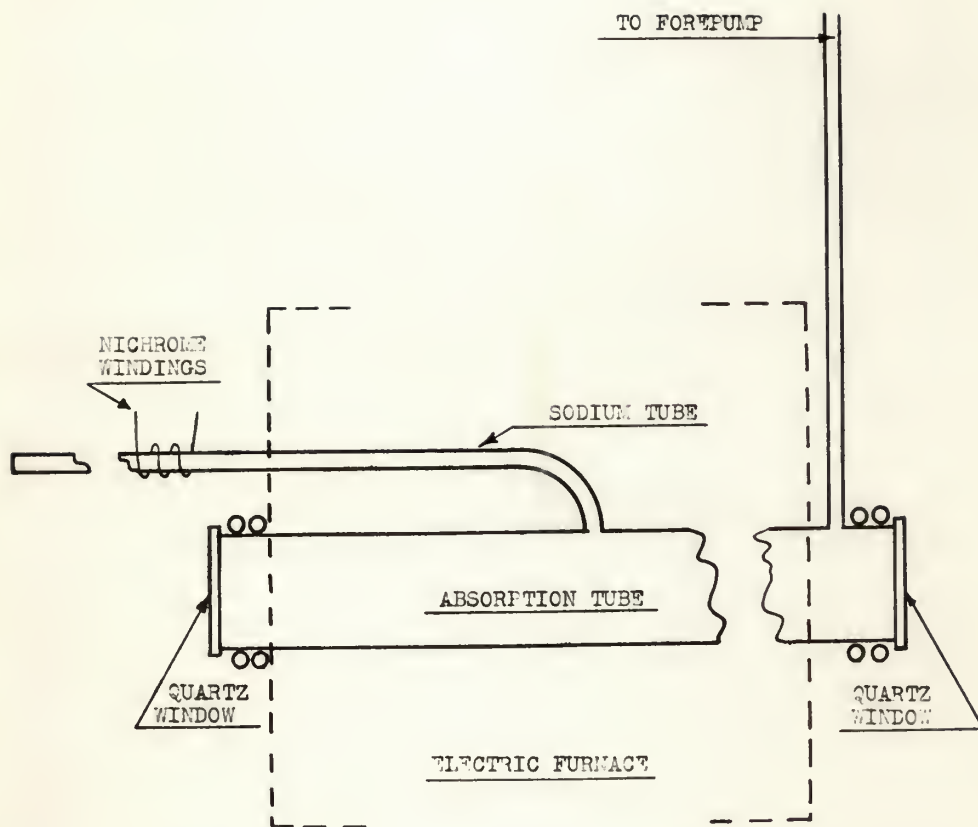
The absorption tube is shown in diagram on Plate II. The main tube, constructed of nickel tubing, was 2.5 centimeters in diameter and was 53 centimeters in length. Since sodium distills at a much lower temperature than lithium and also as it was desired to control the temperatures (and therefore the vapor pressures) of the two metals individually, it was necessary to construct a separate tube for the sodium. This tube was of one-fourth inch diameter nickel tubing which was nickel welded on the center of the main tube. The outer extremity of the tube was closed with silver solder. At such time when it was desired to reopen the tube, the tip was removed with cutters. Quartz windows were waxed to the ends of the absorption tube. The ends of the tube were water cooled to maintain the wax joint and to effect condensation of the metallic vapor prior to the time it settled on the windows. The latter was highly desirable in view of the fact that the alkali metals, especially lithium, attack glass and quartz vigorously at higher temperatures.

Furnace

The absorption tube was mounted in an electric furnace. The side or sodium tube protruded from this furnace and was itself separately wound with nichrome windings. Two variacs were used to control the current through the heating elements. The temperatures were measured with the use of two thermocouples. These

EXPLANATION OF PLATE II
Diagram of the absorption tube

PLATE II



were placed at the center in contact with the nickel tubes.

EXPERIMENTAL PROCEDURE

The general procedure was as follows: First, the absorption spectra of sodium and lithium were observed individually. Second, the spectra of the mixed vapors were observed. Any new band system appearing in the latter spectrograms not identifiable by reference to the spectrums of Na_2 or Li_2 should then be attributable to the metallic combination NaLi .

Preparation of Material

The sodium and lithium were obtained from commercial supply sources. The sodium was ordinary lump sodium metal. Upon receipt at the laboratory, it was divided, placed in glass tubes which were then evacuated, and sealed off at forepump pressure. When it was desired to place a sodium load in the absorption cell, a glass tube was broken and the sodium transferred.

The lithium was delivered to the laboratory in small vials containing one gram of lithium each. The metal in the vials was submerged in kerosene. It was stored in this state until time for use. It was then removed, washed with benzene, dried with filter paper, and placed in the absorption cell.

Both sodium and lithium oxidize very rapidly when exposed to the air. For this reason it was necessary to perform the loading, resealing, and evacuation as rapidly as possible. Since an oxide coating was formed on both metals almost instantaneously,

it was impossible to get the loading accomplished without oxidation by this method. The presence of the coating did not prohibit the appearance of the sodium and lithium band system.

Use of Neon

Neon gas was admitted to the absorption tube during all trials. The purpose of the admission of the gas was twofold. First, it was highly desirable as a means of reducing the mean free path and thus prevent undue transfer of the metallic vapors to the cool ends of the tube where condensation on the walls and windows could occur. Second, the presence of gas enhances the probability of the three-body collision necessary for molecular formation.

Neon pressure used was approximately one millimeter of mercury. Pressures of less than one millimeter were tried, but distillation to the quartz windows became so rapid that at 0.5 millimeter of mercury the windows fogged before the series of spectrograms desired were completed.¹

Lithium Trials

Since a considerably higher temperature was necessary to maintain sufficient vapor pressure for lithium than for sodium,

¹Fogged windows were removed with a minimum of heat and washed in benzene and alcohol. This treatment completely cleared the alkali deposit from the quartz and allowed reusage.

it was decided to investigate the lithium absorption first. The absorption cell was attached to the vacuum system and outgassed by evacuation during periods of heating. With the mercury pumps engaged the pressure obtained was near 10^{-5} millimeters of mercury as evidenced by a McLeod gauge. At this point the cell was opened by removing one of the quartz windows and one or more pellets (approximately one-half gram) of lithium were placed in a shallow boat at the center of the absorption cell. The window was then resealed and the cell evacuated. As soon as a proper vacuum was obtained, the system was flushed with neon, re-evacuated, and thence filled with neon to a pressure of approximately one millimeter of mercury. The tube was then heated and the absorption spectrograms taken. Highest temperatures used were in the neighborhood of 850°C . Work above this temperature was attempted but it was found that the lithium load distilled too rapidly and soon necessitated replenishment.

Sodium Trials

After the lithium trials the tube was opened and washed thoroughly with water. Because strong sodium bands are apparent at a temperature well below the initial temperature at which the lithium 6707 \AA resonance line is evident, it was possible to use the same absorption cell for work with sodium. There was thus little possibility of an absorption from a lithium impurity.

After again outgassing the cell the sodium tube was opened to admit a load (again about one-half gram) of sodium and quickly resealed with silver solder. The cell was then re-evacuated, flushed, and filled with neon as previously described. Temperatures used for the sodium tube varied from 400°C to 550°C . The absorption tube was held at a temperature slightly higher than the sodium tube throughout a trial. During the heating period the use of an ordinary tungsten bulb facilitated the proper choice of exposure. If light from this source was allowed to pass through the absorption tube, a slight greenish or yellow-greenish tinge appeared at temperatures of near 425°C . Approximately, the appearance of the sodium band system coincided with this phenomena. At higher temperatures, the light appeared a darker greenish cast and, correspondingly, was associated with strong absorption.

Combination Trials

The sodium-lithium combination trials were most critical. As was pointed out earlier, it was necessary to try working with a heavy concentration of lithium vapor associated with a trace of sodium and vice versa in an attempt to bring out a NaLi band structure possibly superimposed on a Na_2 or Li_2 band system. This necessitated accurate temperature control.

Preparation and loading for the combination trials proceeded as in the individual sodium and lithium trials. Three mixture ratios were tried. First, the sodium and lithium were heated in

a manner so that there was an abundance of both vapors existing simultaneously in the absorption cell. Second, the lithium was heated to near 350°C producing an abundance of lithium vapor. The sodium tube was then heated to allow various concentrations of the sodium with the lithium vapor. Third, the sodium vapor was produced in abundance and the lithium was heated to produce varying ratios of lithium vapor to sodium vapor.

EXPERIMENTAL RESULTS

During the trials in which lithium was the largest constituent, the lithium load was depleted quite rapidly. This necessitated the reopening and subsequent cleaning of the tube. The tube was cleaned and outgassed prior each trial. This was required since heating of the absorption tube vaporized any sodium previously distilled into it and prevented proper control of the sodium vapor pressure.

Some difficulty was encountered in the choice of appropriate temperatures of the two tubes. Both metals formed an oxide jacket in the process of loading and evacuation. This jacket apparently forms a barrier for the metal. Varying temperatures were required before the vapor pressure became sufficient to break this barrier and allow the vapor to diffuse easily into the cell. Indeed, lithium remained in lump form until about 700°C even though the pure metal has a melting point of only 186°C .

EXPLANATION OF PLATE III

- Fig. 1. Reproduction of a spectrographic plate showing the red and the blue-green band systems of the lithium molecule. The seven exposures were made at 50°C intervals beginning with the lower exposure which was taken at a temperature of 600°C. The blue-green system and the lithium 6707 Å line is evident at 650°C, and gives strong absorption at 700°C. The relatively underexposed spectra above the scale were necessary to bring out the red band system. This system is seen to the right and left of the resonance line in the exposures made at 750°C and 800°C. The two top exposures made at a furnace temperature of 850°C and 900°C show diminishing intensity of the absorption. This was due to the exhaustion of the lithium load by virtue of rapid distillation to the ends of the tube. The source was the 500 watt projection bulb.
- Fig. 2. Reproduction of a spectrographic plate showing the red and the blue-green band systems of the sodium molecule. The seven exposures were made with the temperatures of the sodium tube and the absorption tube at the temperatures indicated to the right of the photograph. The central exposure was made using an incandescent source. The remaining exposures were made using the mercury arc as source. The band systems in the red, blue green, and violet are shown.
- Fig. 3. Reproduction of a spectrographic plate showing the absorption resulting from the vapors of combinations of the two metals. This plate was chosen since it shows a variety of mixtures of the two elements. The lower two spectrograms show an abundance of sodium. This resulted from vaporization of sodium which had previously distilled into the main tube. The upper four exposures were made with an abundance of the lithium vapors and increasing (upwards) amounts of the sodium vapors. Unfortunately, the absorption in the red portion of the exposures has been partially lost in the development. The temperature of the main furnace is given to the right of the figure; the temperature of the sodium tube is given to the left of the figure.

PLATE III

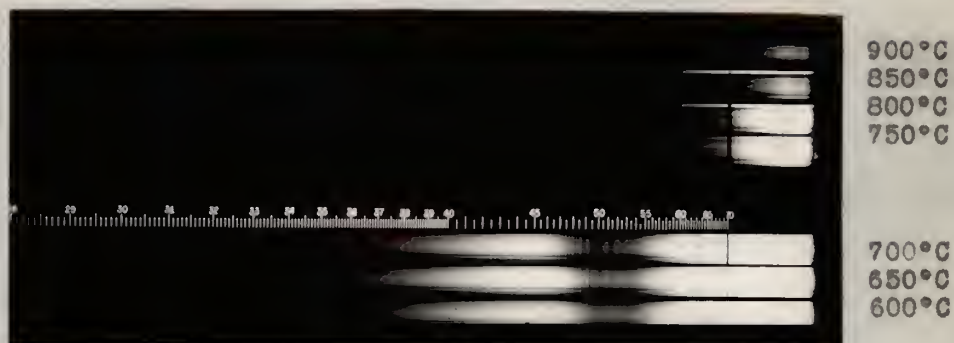


Fig. 1

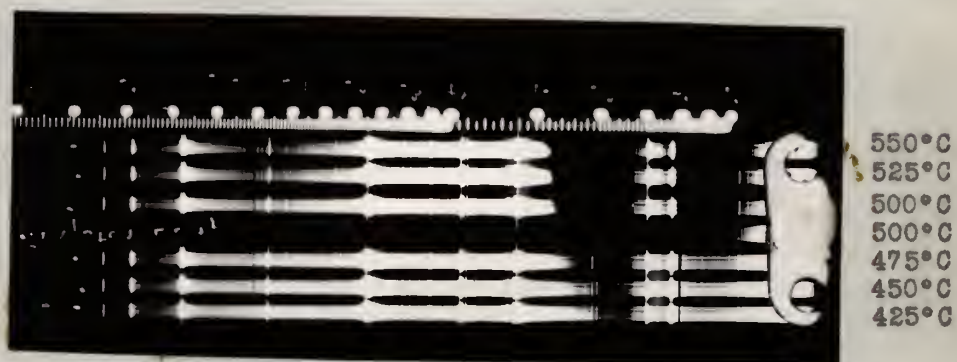


Fig. 2

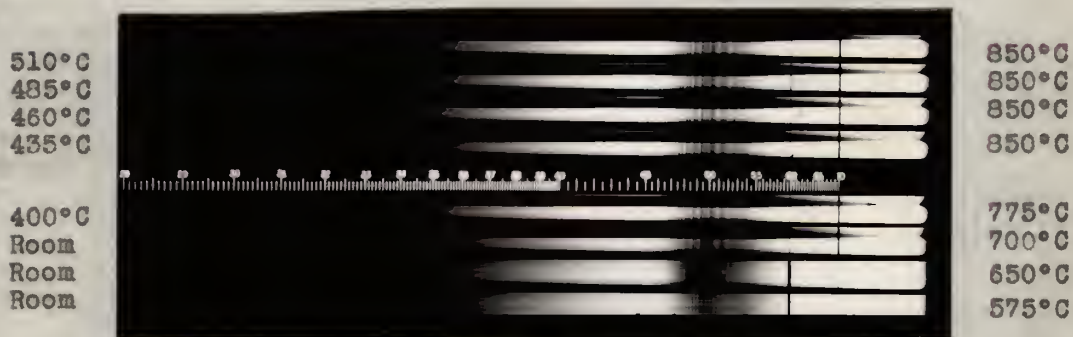


Fig. 3

Plate III shows photographs of the spectrums of lithium, sodium, and sodium-lithium trials taken on the Bausch and Lomb medium quartz spectrograph. The exposures were taken at various pressures of the absorbing gas. Fig. 1 of Plate III shows the two band systems of lithium. The system in the red is brought out in the exposures of lesser intensity. This is also true in the case of Fig. 2 of Plate III showing the spectrum of sodium. The sodium-lithium plate on Fig. 3 of Plate III was chosen because of the varied ratios of the constituent vapors as indicated by the breadth of the resonance lines. The plates show a slight decrease in background intensity in the region from 4900 Å to 5500 Å. This was due to a decrease in the sensitivity of the type I-N plates.

Close examinations of the spectrums yield no lines evident on the combination trial which is not explained by reference to one of the sodium or lithium plates.

CONCLUSION

The results indicate that no NaLi molecule is discernable within the limits of the experimental techniques involved. There is a disadvantage inherent to this study in that the blue-green bands of the two metals are nearly superimposed on one another. The red band systems also overlap to a lesser extent. The spectras of the combination trials are therefore quite complex.

It is felt that the following would be experimental improvements and would aid the investigation:

1. A longer absorption tube.
2. A method whereby the metals could be distilled, in vacuo, into their respective portions of the tube.
3. Glass to metal seals for the end of the absorption tube.

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LITERATURE CITED

- (1) Walter, J. M. and S. Barratt.
The existence of intermetallic compounds in the vapour state, the spectra of the alkali metals, and of their alloys. Proc. Royal Soc. of London, 119 Series A: 257-275. 1928.
- (2) Loomis, F. W. and R. E. Nussbaum.
The magnetic rotation spectrum and the heat of dissociation of the lithium molecule. Phys. Rev. 38: 1447-1457. 1931.
- (3) Harvey, A. and F. A. Jenkins.
Alternating intensities and isotope effect in the blue-green bands of Li_2 . Phys. Rev. 35: 789-801. 1930.
- (4) Wurm, K.
Über die Struktur der roten Lithiumbande. Ztschr. F. Phys. 59: 35-41. 1930.
- (5) Wurm, K.
Über die Rotationsstruktur der blaugrünen Lithiumbande. Ztschr. F. Phys. 58: 562-569. 1929.
- (6) Wood, R. W.
Fluorescence and magnetic rotation spectra of sodium vapor, and their analysis. Am. Acad. Proc. 42: 325-260. 1906.
- (7) Loomis, F. W. and R. E. Nussbaum.
Magnetic rotation spectrum and heat of dissociation of the sodium molecule. Phys. Rev. 40: 380-386. 1932.
- (8) Loomis, F. W.
Vibrational levels and heat of dissociation of Na_2 . Phys. Rev. 31: 323-332. 1928.
- (9) Loomis, F. W. and R. W. Wood.
The rotational structure of the blue green bands of Na_2 . Phys. Rev. 32: 223-236. 1928.
- (10) Loomis, F. W. and P. Kusch.
The band spectrum of cesium. Phys. Rev. 46: 292-301. 1934.
- (11) Loomis, F. W. and M. J. Arvin.
The band spectrum of NaK . Phys. Rev. 46: 286-291. 1934.
- (12) Kusch, P.
The band spectra of rubidium and of its combinations with other alkali metals. Phys. Rev. 49: 218-222. 1936.

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